Rhodium-Catalyzed Regio- and Stereoselective Addition of Diphenylphosphine Oxide to Alkynes

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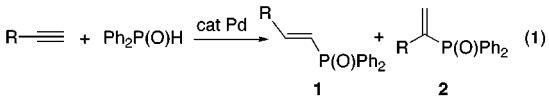
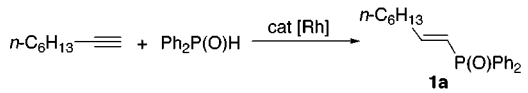
Received March 30, 2001

Alkenylphosphine oxides are useful compounds in numerous synthetic transformations. For example, heteroatom nucleophiles of alcohols,[1] thiols,[2] primary and secondary amines,[3] and phosphines[4] readily add to the olefinic bond in alkenylphosphine oxide to give useful bifunctional adducts, which allow further synthetic elaboration. Carbon−carbon bond formation is also achieved via reactions with carbanion species[5] or carbon-centered radicals.[6] Thus, a wide spectrum of practical applications have been found in the derivatives of alkenylphosphine oxides, including biologically active compounds,[7] fire-retardants,[8] and ligands for homogeneous catalysts.[3d,4b] Despite these diverse applications, methods for their preparation are limited.[9] The recently revealed metal-catalyzed addition of P(V)−H bonds to alkynes provided a new clean methodology for the generation of alkenylphosphorus compounds.[10] Diphenylphosphine oxide added to alkynes in the presence of palladium catalysts to give alkenylphosphine oxides (eq 1).[11a] However, this reaction only slowly proceeded at ambient temperature, affording a mixture of regioisomers **1** and **2**.mployed.[12] Here, we found that rhodium is a novel catalyst which enables the addition of diphenylphosphine oxide to a variety of alkynes, producing the corresponding (*E*)-alkenylphosphine oxides **1** exclusively in excellent yields even at room temperature.



As shown in Table 1, when a mixture of diphenylphosphine oxide and an equimolar amount of phenylacetylene in toluene was stirred in the presence of 3 mol % RhCl(PPh$_3$)$_3$ at room temperature for 1 h, a yellow transparent solution was obtained, where **1a** was formed exclusively in 70% yield. Other halogen-exchanged Willkinson-type catalysts, RhX(PPh$_3$)$_3$ (X = Br, I), exhibit higher catalytic activity. Thus, the yield of **1a** increased to 95% with RhBr(PPh$_3$)$_3$ catalyst, and **1a** was obtained in quantitative yield when RhI(PPh$_3$)$_3$ was e At room temperature, CO-ligated Rh(I)−PPh$_3$ complexes, such as RhCl(CO)(PPh$_3$)$_2$ and RhH(CO)(PPh$_3$)$_3$, were totally ineffective;

Table 1. Hydrophosphinylation of 1-Octyne[a]



catalyst	conditions[a]	% NMR yield
RhCl(PPh$_3$)$_3$	25 °C, 1 h	70
RhBr(PPh$_3$)$_3$		95
RhI(PPh$_3$)$_3$		100
RhCl(CO)(PPh$_3$)$_2$	80 °C, 0.5 h	89[b]
RhH(CO)(PPh$_3$)$_3$	80 °C, 0.5 h	87[b]
[RhCl(cod)]$_2$	25 °C, 1 h	65
Rh(CO)$_2$(acac)	80 °C, 1.5 h	32[b]
Rh(CH$_2$=CH$_2$)(acac)	80 °C, 1.5 h	67[b]
[Rh(OAc)$_2$]$_2$	80 °C, 1.5 h	12[b]
RhCl$_3$	80 °C, 3 (0.5) h[c]	97 (35)[b]
Rh/C[d]	110 °C, 6 h	93

[a] An equimolar mixture of Ph$_2$P(O)H (0.10 mmol) and 1-octyne (0.10 mmol) in toluene−d_8 (0.50 mL) in the presence of 3 mol % [Rh]. [b] No adduct at 25 °C within 2 h. [c] EtOH (0.20 mL) and Et$_3$N (4.0 mL) were added. [d] 5 wt % Rh on activated carbon.

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(12) Other possible isomers could not be found from the crude reaction mixture by 500 MHz ^{1}H NMR spectroscopy.

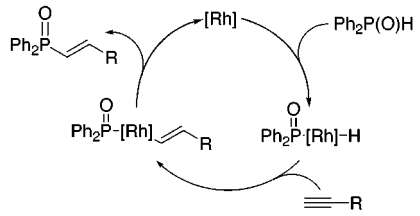
10.1021/jo010337z CCC: $20.00
Published on Web 07/26/2001

however, upon heating at 80 °C, these complexes rapidly gave the adduct in 89% and 87% yields, respectively, in 0.5 h. Note that phosphine-free rhodiums, such as [Rh(cod)Cl]$_2$, also showed good catalytic activity as efficient as RhCl(PPh$_3$)$_3$. Accordingly, the adduct **1a** could be easily generated in high yields by using, for example, either RhCl$_3$ or even a metallic rhodium loaded on carbon as catalyst.

This Rh-catalyzed hydrophosphinylation can be readily applied to a variety of alkynes, proving to be a practically useful method for the selective synthesis of (*E*)-alkenylphosphine oxides which are not readily available by conventional methods (Table 2).[9] Thus, both aliphatic and aromatic terminal alkynes reacted efficiently affording the (*E*)-adducts by the regioselective addition of the phosphorus atom at the terminal carbon of the triple bond in high yields. In addition, a variety of functionalities such as chloro, cyano, amino, alkoxycarbonyl, hydroxyl, silyl, thienyl, and ferrocenyl groups were all tolerant under the present reaction conditions, and the corresponding novel alkenylphosphine oxides were obtained readily.[13] 1-Ethynylcyclohexene underwent hydrophosphinylation exclusively at the triple bond, and an alkene moiety was inert under the present reaction conditions. The formation of the *anti*-Markovnikov β-adduct from 1-ethynylcyclohexene is noteworthy since the related Pd-catalyzed reaction gave the Markovnikov α-adduct instead.[11a,14] As exemplified by run 14, two phosphinyl groups were easily introduced into diynes such as nona-1,8-diyne. Though heating was needed, an internal alkyne could also be successfully hydrophosphinylated producing the corresponding *trans*-adduct selectively.

Although mechanistic aspects remain to be elucidated, it is tentatively proposed that oxidative addition of the P−H bond to rhodiums triggers the reaction[15] (Scheme 1). In fact, upon mixing an equimolar amount of RhCl(PPh$_3$)$_3$ with Ph$_2$P(O)H in CD$_2$Cl$_2$ immediately gave the complex showing a broad singlet at −16.2 ppm in ^{1}H NMR spectroscopy which, as discussed below, may be assigned to PPh$_3$-ligated Rh−H species. When more Ph$_2$P(O)H was used (8 equiv related to Rh), the signal at −16.2 ppm decreased and several new signals emerged at −8.1 ppm (ddq, J = 8.2, 15.5, 186.4 Hz) and −12.4 ppm (doublet of quintet, J = 13.7, 21.0 Hz). These new signals at −8.1 and −12.4 ppm (but not that at −16.2 ppm) could be also observed in a reaction of [RhCl(cod)]$_2$ with Ph$_2$P(O)H, strongly indicating that they are PPh$_3$-free Ph$_2$P(OH)-ligated[15] Rh−H species. Since similar catalytic performance is observed for [RhCl(cod)]$_2$ and RhCl(PPh$_3$)$_3$, it is assumed that these PPh$_3$-free Rh−H species, rather than the PPh$_3$-ligated ones, are the active species in the catalytic reaction.

Scheme 1. Proposed Mechanism



In conclusion, a new convenient and clean method for the preparation of *(E)*-alkenylphosphine oxides has been developed by novel rhodium-catalyzed regio- and stereoselective hydrophosphinylation of alkynes. Applications of the reaction are readily expected on the basis of the well-established synthetic utilities of alkenylphosphine oxides.

Experimental Section

Alkynes are either commercially available or prepared by a reported procedure.[16] They were dried and distilled before use. Diphenylphosphine oxide was purchased from Aldrich and purified by sublimation under a reduced pressure. RhX(PPh$_3$)$_3$ (X = Br, I) were prepared as described in the literature.[17] Other rhodium catalysts were obtained commercially and used without further purification. Solvents were dried and purified under nitrogen before use by standard procedure. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker ARX-300 instrument (300 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P NMR spectroscopy) and/or a JEOL LA-500 instrument (500 MHz for ^{1}H, 125.4 MHz for ^{13}C, and 201.9 MHz for ^{31}P NMR spectroscopy). Unless otherwise noted, CDCl$_3$ was used as the solvent. Chemical shift values for ^{1}H and ^{13}C are referenced to Me$_4$Si (0 ppm), and these for ^{31}P are referenced to H$_3$PO$_4$ (85% solution in D$_2$O, 0 ppm). Melting points were measured on a Yanagimoto Micro Melting Point apparatus (serial no. 331) and were not corrected. Elemental and HRMS analysis were performed by the Analytical Center at the National Institute of Materials and Chemical Research.

Catalytic Addition of Ph$_2$P(O)H to Alkynes: A Representative Procedure. Diphenylphosphine oxide (404 mg, 2.0 mmol), 1-octyne (220 mg, 2.0 mmol), and RhBr(PPh$_3$)$_3$ (58 mg, 3 mol %) were dissolved in 2.0 mL of dry toluene under nitrogen. The resulting transparent yellow solution was stirred at room temperature for ca. 40 min. The solvent was evaporated under a reduced pressure to give a yellow semisolid. The crude product was then purified by column chromatography (SiO$_2$, EtOAc/hexane = 1/1). The colorless oil obtained slowly solidified on standing to give a white solid of **1a** in 91% yield (568 mg). **(*E*)-1-(Diphenylphosphinyl)-1-octene (1a).**[11a] ^{1}H NMR (C$_6$D$_6$) δ 7.78−7.85 (m, 4H), 7.05−7.08 (m, 6H), 6.87−7.01 (m, 1H), 6.11 (dd, 1H, J = 16.9, J_{HP} = 25.1 Hz), 1.87−1.91 (m, 2H), 1.09−1.21 (m, 8H), 0.82 (t, 3H, J = 6.8 Hz); ^{13}C NMR (C$_6$D$_6$) δ 152.2 (J_{CP} = 1.7 Hz), 135.4 (J_{CP} = 92.9 Hz), 131.6 (J_{CP} = 9.5 Hz), 131.3 (J_{CP} = 2.7 Hz), 128.5 (J_{CP} = 11.7 Hz), 123.1 (J_{CP} = 101.8 Hz), 34.6 (J_{CP} = 16.6 Hz), 31.8, 29.1, 28.1, 22.9, 14.2; ^{31}P NMR (C$_6$D$_6$) δ 18.9.

(*E*)-1-(Diphenylphosphinyl)-3,3-dimethyl-1-butene (1b). White solid; mp 157−158 °C; ^{1}H NMR δ 7.64−7.68 (m, 4H), 7.42−7.51 (m, 6H), 6.76 (dd, 1H, J = 17.4, J_{HP} = 24.7 Hz), 6.09 (dd, 1H, J = 17.4, J_{HP} = 20.4 Hz), 1.09 (s, 9H); ^{13}C NMR δ 162.4, 133.4 (J_{CP} = 104.5 Hz), 131.6 (J_{CP} = 2.1 Hz), 131.3 (J_{CP} = 10.4

(13) Under similar conditions, however, methyl propiolate failed to give the corresponding alkenylphosphine oxide. The reaction of methyl propiolate only sluggishly proceeded at room temperature (<5% consumption of the starting materials after 2 h); upon heating at 60 °C, side reactions such as the oligomerization of methyl propiolate took place severely to give a complicated reaction mixture, in which the corresponding alkenylphosphine oxide could not be found at all.

(14) The reason for the different regioselectivity between palladium and rhodium is not clear. It is noted, however, that a similar phenomenon was also observed in a related hydrophosphorylation reaction using a five-membered hydrogen phosphonate as the substrate (ref 10e). In addition, though phosphinic acid can reverse the regioselectivity of the palladium catalyzed hydrophosphinylations (ref 11b), similar effect was not observed in this rhodium catalyzed system.

(15) See ref 10 for related oxidative addition of H−P bonds to metal complexes. Secondary phosphine oxides exist in two tautomeric isomers, P(=O)H and P−OH, which can coodinate to metals. See: (a) Bailey, W. J.; Fox, R. B. *J. Org. Chem.* **1963**, *28*, 531. (b) Bailey, W. J.; Fox, R. B. *J. Org. Chem.* **1964**, *29*, 1013. (c) Roundhill, D. M.; Sperline, R. P.; Beaulieu, W. B. *Coord. Chem. Rev.* **1978**, *26*, 263. (d) Hamilton, L. A.; Landis, P. S. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley: New York, 1972; Vol. 4, Chapter 11.

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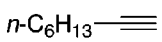
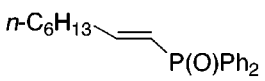
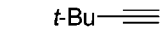
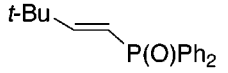
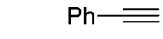
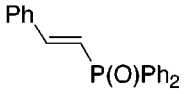
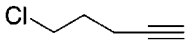
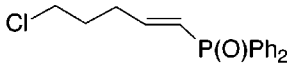
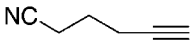
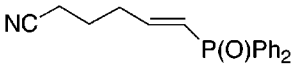
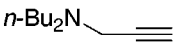
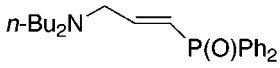
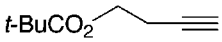
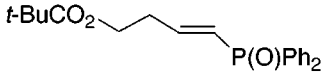
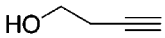
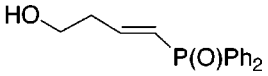
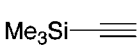
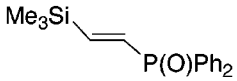
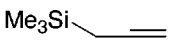
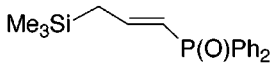
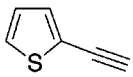
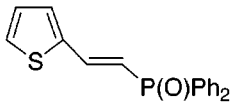
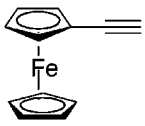
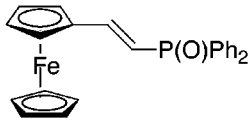
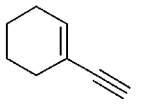
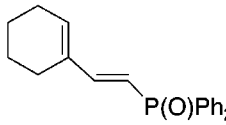
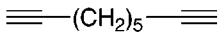
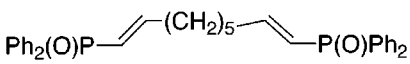
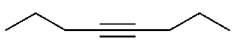
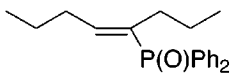
Table 2. Hydrophosphinylation of Alkynes[a]

run	alkyne	conditions	adduct	% isolated yield (NMR yield)
1		rt, 40 min	 (**1a**)	91 (97)
2		rt, 40 min	 (**1b**)	93 (99)
3		rt, 2 h	 (**1c**)	89 (99)
4		rt, 4 h	 (**1d**)	88 (96)
5		60 °C, 12 h	 (**1e**)	92 (96)
6		60 °C, 12 h	 (**1f**)	86 (97)
7		60 °C, 4 h	 (**1g**)	87 (96)
8		rt, 3 h	 (**1h**)	94 (98)
9		60 °C, 12 h	 (**1i**)	85 (93)
10		60 °C, 12 h	 (**1j**)	81 (93)
11		60 °C, 4.5 h	 (**1k**)	92 (99)
12		rt, 2 h	 (**1l**)	93 (98)
13		rt, 2 h	 (**1m**)	94 (99)
14		60 °C, 4 h	 (**1n**)	76 (91)
15		100 °C, 2 h	 (**1o**)	91 (95)

[a] Reaction conditions: an equimolar amount of $Ph_2P(O)H$ and an alkyne in toluene (1 M), 1∼3 mol % $RhBr(PPh_3)_3$.

Hz), 128.5 (J_{CP} = 11.4 Hz), 116.4 (J_{CP} = 103.4 Hz), 35.2 (J_{CP} = 14.5 Hz), 28.7; ^{31}P NMR δ 24.2. Anal. Calcd for $C_{18}H_{21}OP$: C, 76.04; H, 7.44. Found: C, 75.83; H, 7.42. HRMS Calcd for $C_{18}H_{21}OP$: 284.1330; found: 284.1275.

(*E*)-1-(Diphenylphosphinyl)-2-phenylethene (1c).[11a] ^1H NMR δ 7.37−7.38 (m, 16H), 6.83 (dd, 1H, J = 17.3, J_{HP} = 22.3 Hz); ^{31}P NMR δ 24.4.

(*E*)-5-Chloro-1-(diphenylphosphinyl)-1-pentene (1d). White solid; mp 93−94 °C; ^1H NMR δ 7.63−7.67 (m, 4H), 7.41−7.50 (m, 6H), 6.69 (ddt, 1H, J = 6.4, 17.1, J_{HP} = 19.2 Hz), 6.29 (dd, 1H, J = 17.1, J_{HP} = 24.4 Hz), 3.50−3.52 (m, 2H), 2.44−2.45 (m, 2H), 1.91−1.93 (m, 2H); ^{13}C NMR δ 150.4, 133.0 (J_{CP} = 104.5 Hz), 131.8 (J_{CP} = 2.0 Hz), 131.3 (J_{CP} = 10.3 Hz), 128.6 (J_{CP} = 11.6 Hz), 122.8 (J_{CP} = 102.4 Hz), 44.1, 31.5 (J_{CP} = 16.6

Hz), 30.6; ^{31}P NMR δ 23.0. Anal. Calcd for $C_{17}H_{18}ClOP$: C, 67.00; H, 5.95. Found: C, 67.02; H, 5.88. HRMS Calcd for $C_{17}H_{18}ClOP$: 304.0784; found: 304.0785.

(*E*)-5-Cyano-1-(diphenylphosphinyl)-1-pentene (1e).[11a] ^{1}H NMR (C_6D_6) δ 7.40−7.78 (m, 10H), 6.58−6.70 (m, 1H), 6.30 (dd, 1H, J = 17.0, J_{HP} = 24.2 Hz), 2.38−2.45 (m, 2H), 2.30 (t, 2H, J = 7.0 Hz), 1.76−1.83 (m, 2H); ^{13}C NMR (C_6D_6) δ 149.1 (J_{CP} = 2.1 Hz), 132.9 (J_{CP} = 92.0 Hz), 131.9 (J_{CP} = 2.7 Hz), 131.2 (J_{CP} = 10.0 Hz), 128.6 (J_{CP} = 12.1 Hz), 124.3 (J_{CP} = 101.2 Hz), 119.0, 32.9 (J_{CP} = 7.1 Hz), 23.7, 16.6; ^{31}P NMR (C_6D_6) δ 22.6.

(*E*)-3-(Dibutylamino)-1-(diphenylphosphinyl)-1-propene (1f). White solid; mp 84−86 °C; ^{1}H NMR δ 7.63−7.68 (m, 4H), 7.41−7.49 (m, 6H), 6.64−6.73 (m, 1H), 6.49 (dd, 1H, J = 17.1, J_{HP} = 24.1 Hz), 3.26 (bs, 2H), 2.40 (t, 4H, J = 7.6 Hz), 1.34−1.40 (m, 4H), 1.20−1.27 (m, 4H), 0.84 (t, 6H, J = 7.6 Hz); ^{13}C NMR δ 150.1, 133.0 (J_{CP} = 104.5 Hz), 131.7 (J_{CP} = 2.1 Hz), 131.3 (J_{CP} = 10.4 Hz), 128.5 (J_{CP} = 12.4 Hz), 123.5 (J_{CP} = 104.5 Hz), 57.1 (J_{CP} = 17.6 Hz), 54.2, 29.4, 20.6, 14.1; ^{31}P NMR δ 23.8. Anal. Calcd for $C_{23}H_{32}NOP$: C, 74.77; H, 8.73; N, 3.79. Found: C, 74.37; H, 8.74; N, 3.66. HRMS Calcd for $C_{23}H_{32}NOP$: 369.2222; found: 369.2250.

(*E*)-4-(Diphenylphosphinyl)-3-butenyl 2,2-dimethylpropanoate (1 g). White solid; mp 103−104 °C; ^{1}H NMR δ 7.63−7.68 (m, 4H), 7.41−7.51 (m, 6H), 6.63−6.73 (m, 1H), 6.31 (dd, 1H, J = 17.1, J_{HP} = 23.8 Hz), 4.18 (t, 2H, J = 6.4 Hz), 2.60−2.63 (m, 2H), 1.08 (s, 9H); ^{13}C NMR δ 178.4, 147.7, 132.6 (J_{CP} = 105.5 Hz), 131.8 (J_{CP} = 3.1 Hz), 131.2 (J_{CP} = 9.3 Hz), 128.5 (J_{CP} = 12.4 Hz), 124.6 (J_{CP} = 102.4 Hz), 62.1, 38.7, 33.6 (J_{CP} = 17.6 Hz), 27.1; ^{31}P NMR δ 23.2. Anal. Calcd for $C_{21}H_{25}O_3P$: C, 70.77; H, 7.07. Found: C, 70.52; H, 7.03. HRMS Calcd for $C_{21}H_{25}O_3P$: 356.1541; found: 356.1555.

(*E*)-1-(Diphenylphosphinyl)-4-hydroxy-1-butene (1h).[11a] ^{1}H NMR δ 7.26−7.69 (m, 10H), 6.64−6.76 (m, 1H), 6.30 (dd, 1H, J = 17.2, J_{HP} = 24.6 Hz), 3.69 (t, 2H, J = 6.3 Hz), 3.67 (bs, 1H), 2.42−2.53 (m 2H); ^{13}C NMR 149.7 (J_{CP} = 2.2 Hz), 132.7 (J_{CP} = 105.3 Hz), 131.8 (J_{CP} = 2.7 Hz), 131.2 (J_{CP} = 10.0 Hz), 128.6 (J_{CP} = 12.1 Hz), 123.6 (J_{CP} = 102.5 Hz), 60.4 (J_{CP} = 1.3 Hz), 37.8 (J_{CP} = 16.7 Hz); ^{31}P NMR δ 24.1.

(*E*)-1-(Diphenylphosphinyl)-2-trimethylsilylethene (1i). White solid; mp 113−114 °C; ^{1}H NMR δ 7.64−7.68 (m, 4H), 7.41−7.51 (m, 6H), 7.25 (dd, 1H, J = 20.4, J_{HP} = 29.5 Hz), 6.82 (dd, 1H, J = 20.4, J_{HP} = 32.7 Hz), 0.13 (s, 9H); ^{13}C NMR δ 155.2, 137.0 (J_{CP} = 91.0 Hz), 132.7(J_{CP} = 102.5 Hz), 131.8 (J_{CP} = 3.1 Hz), 131.4 (J_{CP} = 9.3 Hz), 128.5 (J_{CP} = 12.4 Hz), −1.8; ^{31}P NMR δ 22.8. Anal. Calcd for $C_{17}H_{21}OPSi$: C, 67.97; H, 7.05. Found: C, 67.74; H, 6.98. HRMS Calcd for $C_{17}H_{21}OPSi$: 300.1099; found: 300.1099.

(*E*)-1-(Diphenylphosphinyl)-3-trimethylsilylpropene (1j). White solid; mp 89−90 °C; ^{1}H NMR δ 7.65−7.69 (m, 4H), 7.40−7.48 (m, 6H), 6.68 (ddt, 1H, J = 8.6, 16.7, J_{HP} = 19.6 Hz), 6.01 (dd, 1H, J = 16.7, J_{HP} = 24.4 Hz), 1.82 (d, 2H, J = 8.6 Hz), 0.13 (s, 9H); ^{13}C NMR δ 150.9, 133.7 (J_{CP} = 104.5 Hz), 131.5 (J_{CP} = 3.1 Hz), 131.3 (J_{CP} = 10.4 Hz), 128.5 (J_{CP} = 12.4 Hz), 119.2 (J_{CP} = 106.6 Hz), 27.5 (J_{CP} = 16.6 Hz), −1.7; ^{31}P NMR δ 23.8. Anal. Calcd for $C_{18}H_{23}OPSi$: C, 68.76; H, 7.37. Found: C, 69.12; H, 7.03. HRMS Calcd for $C_{18}H_{23}OPSi$: 314.1256; found: 314.1191.

(*E*)-1-(Diphenylphosphinyl)-2-(2-thienyl)ethene (1k). Pale yellow solid; mp 145−146 °C; ^{1}H NMR δ 7.70−7.75 (m, 4H), 7.41−7.61 (m, 7H), 7.32 (d, 1H, J = 4.9 Hz), 7.16 (d, 1H, J = 3.4 Hz), 6.90−7.08 (m, 1H), 6.56 (dd, 1H, J = 17.1, J_{HP} = 21.3 Hz); ^{13}C NMR δ 140.8 (J_{CP} = 20.7 Hz), 139.9, 132.9 (J_{CP} = 106.6 Hz), 131.9 (J_{CP} = 2.1 Hz), 131.4 (J_{CP} = 9.3 Hz), 130.2, 128.6 (J_{CP} = 12.4 Hz), 128.1, 128.0, 117.8 (J_{CP} = 106.6 Hz); ^{31}P NMR δ 24.1. Anal. Calcd for $C_{18}H_{15}OPS$: C, 69.66; H, 4.87. Found: C, 69.47; H, 4.78. HRMS Calcd for $C_{18}H_{15}OPS$: 310.0581; found: 310.0555.

(*E*)-1-(Diphenylphosphinyl)-2-ferrocenylethene (1l). Brown solid; mp 163−164 °C; ^{1}H NMR δ 7.59−7.63 (m, 4H), 7.30 (dd, 1H, J = 17.1, J_{HP} = 18.3 Hz), 7.16−7.21 (m, 6H), 6.21 (dd, 1H, J = 17.1, J_{HP} = 23.5 Hz), 4.46 (s-like, 2H), 4.34 (s-like, 2H), 4.10 (s, 5H); ^{13}C NMR δ 148.1, 133.5 (J_{CP} = 105.5 Hz), 131.7, 131.3 (J_{CP} = 10.3 Hz), 128.6 (J_{CP} = 12.4 Hz), 115.2 (J_{CP} = 107.6 Hz), 80.1 (J_{CP} = 20.7 Hz), 70.6, 69.6, 68.3; ^{31}P NMR δ 23.7. Anal. Calcd for $C_{24}H_{21}FeOP$: C, 69.92; H, 5.13. Found: C, 69.71; H, 5.04. HRMS Calcd for $C_{24}H_{21}FeOP$: 412.0679; found: 412.0679.

(*E*)-1-(Cyclohexen-1-yl)-2-(diphenylphosphinyl)ethene (1m). White solid; mp 126−128 °C; ^{1}H NMR δ 7.57−7.62 (m, 4H), 7.31−7.41 (m, 6H), 6.92 (dd, 1H, J = 17.4, J_{HP} = 19.5 Hz), 5.97 (dd, 1H, J = 17.4, J_{HP} = 22.5 Hz), 5.96 (bs, 1H), 2.06−2.07 (m, 4H), 1.55−1.60 (m, 2H), 1.47−1.51 (m, 2H); ^{13}C NMR δ 151.0 (J_{CP} = 4.1 Hz), 137.9, 135.2 (J_{CP} = 17.6 Hz), 133.4 (J_{CP} =105.5 Hz), 131.5 (J_{CP} = 2.0 Hz), 131.3 (J_{CP} = 9.3 Hz), 128.4 (J_{CP} = 11.4 Hz), 114.6 (J_{CP} = 106.6 Hz), 26.2, 24.1, 22.0, 22.0; ^{31}P NMR δ 25.3. Anal. Calcd for $C_{20}H_{21}OP$: C, 77.90; H, 6.86. Found: C, 77.61; H, 6.74. HRMS Calcd for $C_{20}H_{21}OP$: 308.1330; found: 308.1325.

(*E*,*E*)-1,9-Bis(diphenylphosphinyl)-1,8-nonadiene (1n).[11a] ^{1}H NMR δ 7.41−7.79 (m, 20H), 6.63−6.70 (m, 2H), 6.20 (dd, 2H, J = 16.9, J_{HP} = 24.6 Hz), 2.22−2.27 (m, 4H), 1.27−1.58 (m, 6H); ^{13}C NMR δ 152.4 (J_{CP} = 1.9 Hz), 133.2 (J_{CP} = 104.8 Hz), 131.7 (J_{CP} = 2.7 Hz), 131.3 (J_{CP} = 10.0 Hz), 128.5 (J_{CP} = 12.0 Hz), 121.8 (J_{CP} = 103.0 Hz), 34.3 (J_{CP} = 16.8 Hz), 28.7, 27.7; ^{31}P NMR δ 23.4.

(*E*)−(4-Diphenylphosphinyl)-4-octene (1o).[11a] ^{1}H NMR δ 7.83−7.89 (m, 4H), 7.06−7.08 (m, 6H), 6.18 (dt, 1H, J = 7.2, J_{HP} = 21.6 Hz), 2.29−2.34 (m, 2H), 1.89−1.93 (m, 2H), 1.47−1.52 (m, 2H), 1.09−1.17 (m, 2H), 0.69−0.77 (m, 6H); ^{13}C NMR δ 146.2 (J_{CP} = 10.1 Hz), 135.3 (J_{CP} = 96.3 Hz), 134.0 (J_{CP} = 99.8 Hz), 132.4 (J_{CP} = 9.3 Hz), 131.4 (J_{CP} = 2.0 Hz), 128.5 (J_{CP} = 11.8 Hz), 30.9 (J_{CP} = 15.4 Hz), 30.6 (J_{CP} = 10.9 Hz), 23.5, 22.4, 14.4, 13.9; ^{31}P NMR δ 29.8.

Acknowledgment. We are grateful to the Japan Science and Technology Corporation (JST) for partial financial support through the CREST (Core Research for Evolutional Science and Technology) program, and for a postdoctoral fellowship to C.-Q.Z. (STA fellow).

JO010337Z